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The Radiolysis of Aqueous Solutions of Potassium Iodide

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The radiolysis of potassium iodide aqueous solutions has been studied in order to elucidate the contribution of the hydrated electrons to the radiolysis mechanisms. The deaerated and aerated solutions were irradiated by ^{60}Co γ-rays under various conditions, and the yields of iodine, hydrogen peroxide, hydrogen and oxygen were determined. The pH dependences of the initial yields of iodine and hydrogen peroxide in the deaerated solutions are different from the results obtained in the aerated solutions. These results can be reasonably explained by assuming the hydrogen atoms and hydrated electrons to be the reducing species. From an examination of the results, the radiolysis mechanisms of the potassium iodide aqueous solutions have been discussed. The rate constant of the reaction of hydrated electrons for iodine has been calculated to be 5.9×10^{10} M^{-1} sec^{-1}.

The radiolysis of aqueous solutions containing iodide ions has already been studied by several workers,[1-5] and it is known that the yields of the products, iodine, hydrogen peroxide, hydrogen and oxygen, depend upon the concentrations of iodide ions, hydrogen ions and oxygen in the solution. Allen et al.[3] observed that the yield of iodine from the radiolysis of the deaerated iodide solution was very low in a neutral and high in a 0.8 N sulfuric acid solution. The radiolysis of an iodide ion solution is known to be an oxidation-reduction reaction, but this system has not yet been completely examined.

Most of the radiation chemical reactions of aqueous solutions have been explained by assuming hydrogen atoms and hydroxyl radicals as the primary intermediates. Recently the existence of two forms of the reducing species has been reported by many authors, and it has been shown that one is a hydrogen atom and the other, a hydrated electron.[6-19]

In the present work, the radiolysis of potassium iodide aqueous solutions has been investigated under various conditions in order to elucidate the contribution of the hydrated electrons to the radiolysis mechanisms.

Experimental

The Preparation of Samples and the Irradiation.—All the materials used were of GR grade, and the solutions were prepared using triply-distilled water. The aerated and deaerated solutions (20 ml.) of various concentrations of potassium idodide, from 5×10^{-4} to 0.1 M, and of various pH values, from 0.5 to about 7, were irradiated by ^{60}Co γ-rays at room temperature. The air-free neutral solutions were obtained by bubbling in nitrogen gas filtered with triply-distilled water and by degassing them using the standard freezing-pumping technique. For the determination of the variation in the oxygen concentration in the irradiated aerated solutions, an irradiation vessel similar to one described by Boyle[20] was used. The pH value was controlled with sulfuric acid and was measured in a nitrogen stream by using a Horiba, model 3, pH meter.

To avoid the thermal oxidation of iodide ions at low pH values, the irradiations were made immediately after mixing the degassed potassium iodide solution with the degassed sulfuric acid solution.

The doses employed were from 1.0×10^{18} to 1.5×10^{19} eV./ml. Dosimetry was carried out by using an aerated solution of 5×10^{-3} M ferrous ammonium sulfate in 0.8 N sulfuric acid.

Analysis.—Iodine was determined from the absorption of tri-iodide ions at 305 mμ by using a Shimadzu QR-50 spectrophotometer and hydrogen peroxide, by Ghormley's method.[21] The gaseous products were collected by means of a Toepler pump, and hydrogen and oxygen were analyzed by gas chromatography (Shimadzu GC-2B) by using a Molecular Sieve 13X column at room temperature. As a carrier gas, argon or hydrogen was used. The hydrogen was also determined by a mass spectrometer (Hitachi RMU-5G).

Results

The Yields of Products in Air-free Neutral Potassium Iodide Solutions.—The formation of iodine, hydrogen peroxide, hydrogen, and oxygen in deaerated neutral solutions of potassium iodide (pH 6.5—6.7) is shown in Fig. 1. The concentrations of iodine and hydrogen peroxide increase with an increase in the dose and reach the steady-state concentrations at about 2×10^{18} eV./ml. The initial G-values of iodine and hydrogen peroxide are 0.10 and 0.13 respectively. The amount of hydrogen produced increases linearly with the dose, and $G(H_2)$ is calculated to be 0.45, which is in good agreement with the "molecular hydrogen yield." Oxygen is formed at doses higher

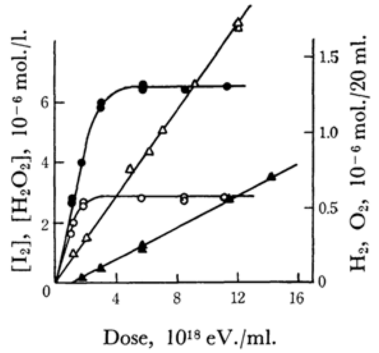

Fig. 1. Yields of products from deaerated potassium iodide aqueous solutions irradiated by ^{60}Co γ-rays.
[KI] : 5×10^{-4} M, pH : 6.5—6.7
● : H_2O_2, ○ : I_2, △ : H_2, ▲ : O_2

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1) F. Fricke and E. J. Hart, *J. Chem. Phys.*, **3**, 596 (1935).
2) E. R. Johnson, ibid., **21**, 1417 (1953).
3) A. O. Allen, J. P. Jr. Losee and H. A. Schwarz, *J. Am. Chem. Soc.*, **76**, 4693 (1954).
4) E. J. Hart and C. B. Senvar, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, **29**, 19 (1958).
5) S. Gordon and E. J. Hart, ibid., **29**, 13 (1958).
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10) E. Collinson, F. S. Dainton, D. R. Smith and S. Tazuké, *Proc. Chem. Soc.*, 140 (1962).
11) J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960).
12) J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1962).
13) J. T. Allan and C. M. Beck, *J. Am. Chem. Soc.*, **86**, 1483 (1964).
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16) E. Hayon, ibid., **61**, 723 (1965).
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18) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani and J. K. Thomas, ibid., **85**, 1375 (1963).
19) J. P. Keene, *Nature*, **197**, 47 (1963).
20) J. W. Boyle, *Rad. Res.*, **17**, 450 (1962).
21) A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Paris, *J. Phys. Chem.*, **56**, 575 (1952).

than 1×10^{18} eV./ml., and the $G(O_2)$ value is 0.17. In the deaerated solution of pH 5.3, the G-values of iodine, hydrogen peroxide, and oxygen are 0.14, 0.27, and 0.22 respectively.

The Effects of the Potassium Iodide Concentration on the Initial Yields of Iodine and Hydrogen Peroxide.—The initial G-values of iodine and hydrogen peroxide in the aerated and deaerated solutions are shown in Fig. 2 as a function of the potassium iodide concentration. With an increase in the iodide ion concentration, the yield of iodine increases and the hydrogen peroxide yield decreases, the formation of hydrogen peroxide reaches a very low steady-state concentration ($\sim1\times10^{-6}$ M) at the higher concentration of iodide ion ($\sim$0.1 M).

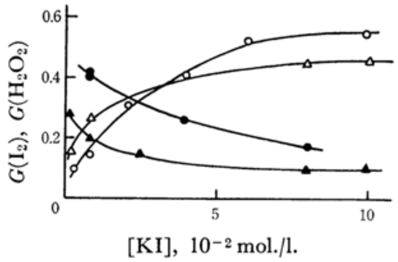

Fig. 2. Effects of potassium iodide concentrations on the initial yields of products in aerated and deaerated solutions at pH 5.3.

○ : I_2 in aerated, ● : H_2O_2 in aerated,
△ : I_2 in deaerated, ▲ : H_2O_2 in deaerated

The Dependence of the Initial Yields on the pH Values.—The pH dependences of the initial yields in the deaerated and aerated iodide solutions of 8.5×10^{-3} M are shown in Figs. 3 and 4. In the deaerated systems, the hydrogen yield decreases with an increase in the pH and becomes constant at about pH 2.5. The iodine yield shows a minimum in the range of pH 2.0—2.5. On the contrary, the yield of hydrogen peroxide shows a maximum in the same pH range. From the results in Fig. 3, it can be seen that, at pH values lower than 2, the change in the $G(I_2)$ with the pH is equal to the sum of the changes in $G(H_2O_2)$ and $G(H_2)$, and that in the higher pH range the change in $G(I_2)$ is equal to the change in $G(H_2O_2)$.

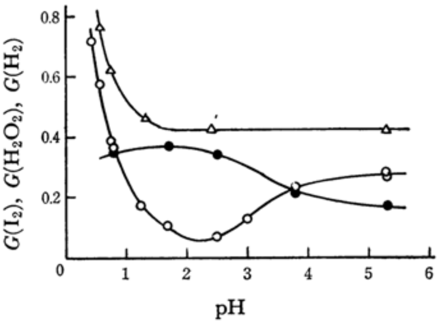

Fig. 3. Effects of pH on the initial yields of I_2, H_2O_2 and H_2 in the radiolysis of deaerated aqueous potassium iodide solutions.

[KI] : 8.5×10^{-3} M
△ : H_2, ○ : I_2, ● : H_2O_2

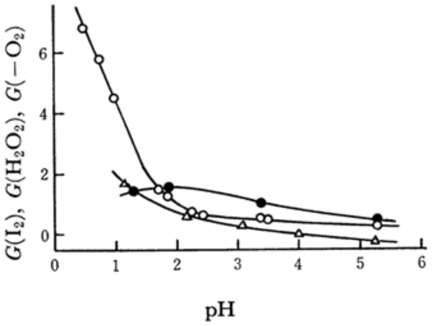

Fig. 4. Effects of pH on the initial yields of I_2, H_2O_2 and $-O_2$ in the radiolysis of aerated aqueous potassium iodide solutions.

[KI] : 8.5×10^{-3} M
○ : I_2, ● : H_2O_2, △ : $-O_2$

In the aerated systems, $G(I_2)$ decreases smoothly with an increase in the pH, as is shown in Fig. 4. $G(H_2O_2)$ shows behavior similar to that of the deaerated systems. With irradiation, the amount of dissolved oxygen increases at pH 5.3 but decreases at pH values lower than 4, while $G(-O_2)$ increases with a decrease in the pH.

Discussion

The Dependence of Initial Yields on the pH.—The radiolysis mechanisms of the aerated iodide solution were proposed by Allen.22) For the deaerated system, however, no definite mechanisms have been given. In the radiolysis of aqueous solutions, hydrogen atoms and hydroxyl radicals have so far been assumed to be the primary intermediates, but the results obtained in these experiments, for example, the pH dependence of $G(I_2)$ or $G(H_2O_2)$, can not be explained only in terms of hydrogen atoms and hydroxyl radicals.

As to the formation of iodine from iodide ions, the following reactions can be postulated:

$$OH + I^- \rightarrow OH^- + I \tag{1}$$

$$2I^- + H_2O_2 \xrightarrow{H^+} 2I + 2H_2O \tag{2}$$

$$I + I \rightarrow I_2 \qquad I + I^- \rightarrow I_2^- \tag{3}$$

$$I_2^- + I_2^- \rightarrow I_3^- + I^- \qquad I_2 + I^- \rightleftarrows I_3^- \tag{4}$$

By assuming a hydrated electron as an intermediate, the results can be explained by the following competitive reactions:

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22) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., New York (1961).

$$e^-_{aq} + H^+ \rightarrow H \tag{5}$$

$$e^-_{aq} + H_2O_2 \rightarrow OH + OH^- \tag{6}$$

$$e^-_{aq} + I \rightarrow I^- \tag{7}$$

In a strongly acidic medium, hydrated electrons are converted to hydrogen atoms by the reaction 5, followed by the reaction 8, which forms hydrogen and iodine:

$$H + I^- + H^+ \rightarrow H_2 + I \tag{8}$$

As the pH increases, the reaction 8 decreases and the reaction 5 is followed by the reaction 9, and thus $G(I_2)$ and $G(H_2)$ decrease:

$$H + I \rightarrow H^+ + I^- \tag{9}$$

From the fact that $G(H_2)$ shows an almost constant value at pH higher than 2.5, it is clear that the *reaction 8 is negligible in this pH range and that the hydrogen atoms produced reduce iodine* atoms by means of the reaction 9. These facts agree with the results of the reaction of iodide ions with atomic hydrogen presented by Stein et al.[23] The oxidation reaction by hydrogen peroxide, which can occur in a strongly acidic medium, also decreases with an increasing pH, resulting in a slight increase in $G(H_2O_2)$:

$$2I^- + H_2O_2 \xrightarrow{H^+} 2I + 2H_2O \tag{2}$$

With a further increase in pH, the reaction 6 becomes important in giving more iodine by the reaction of the hydroxyl radical produced by the reaction 6, and thus $G(I_2)$ increases and $G(H_2O_2)$ decreases. From these mechanisms, the relations between the changes in $G(I_2)$ and $G(H_2O_2)$ with the pH (Fig. 3) can be explained reasonably.

In the aerated solutions, the following reactions are added to the reactions in the deaerated solutions:

$$e^-_{aq} + O_2 \rightarrow O_2^- \tag{10}$$

$$O_2^- + I \rightarrow O_2 + I^- \tag{11}$$

$$O_2^- + H^+ \rightarrow O_2 + H \quad (\text{or } HO_2) \tag{12}$$

$$H + O_2 \rightarrow HO_2 \tag{13}$$

$$HO_2 + I^- + H^+ \rightarrow H_2O_2 + I \tag{14}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{15}$$

With an increasing pH, the reactions 10 and 11 increase and 12, 13, and 14 decrease; thus $G(I_2)$, $G(H_2O_2)$, and $G(-O_2)$ fall smoothly, as is shown in Fig. 4. At pH 5.3 oxygen is formed, as will be described later.

The Dependence of Hydrogen Peroxide Formation on the Potassium Iodide Concentration.—From the dependence of $G(I_2)$, $G(H_2O_2)$ and the stationary concentration of iodine and hydrogen peroxide on the iodide ion concentration, it may be concluded that the hydrogen peroxide oxidizes iodide ions, presumably by the reaction 2. The fact that in the aerated solutions $G(H_2O_2)$ and the steady concentration of hydrogen peroxide are higher than those in the dearated solution, may be explained by the reactions 10, 12, 13, and 14.

Reactions in Deaerated Neutral Solutions.—The reactions 1, 5, 6, 7, and 9 can be assumed in the deareated neutral solution of potassium iodide 5×10^{-4} M, because the concentrations of hydrogen ion and iodide ion are very low. The oxidation reaction by hydrogen peroxide can be neglected in the low concentration range of potassium iodide in a neutral solution.

Oxygen is formed secondarily by the reaction of hydrogen peroxide with iodine. The following mechanisms were suggested by Anbar et al.[24] *for the formation of oxygen in the radiloysis* of potassium iodide solutions saturated with nitrous oxide:

$$I_2^- + H_2O_2 \rightarrow 2I^- + H^+ + HO_2 \tag{16}$$

$$I_3^- + H_2O_2 \rightarrow 3I^- + 2H^+ + O_2 \tag{17}$$

$$I_2 + HO_2 \rightarrow I_2^- + H^+ + O_2 \tag{18}$$

$$I_2^- + HO_2 \rightarrow 2I^- + H^+ + O_2 \tag{19}$$

Since the pK of HO_2 is 4.5 ± 0.2,[25] oxygen may also be produced by the following reactions:

$$HO_2 \rightleftarrows O_2^- + H^+ \tag{20}$$

$$O_2^- + (I, I_2, I_2^-, I_3^-) \rightarrow O_2 \tag{11$'$}$$

The iodine produced is present in the forms of I_2 and I_3^-. If hydrogen peroxide is oxidized by I_2 or I_3^- to oxygen, the variations in the concentrations of hydrogen peroxide and iodine have to be observed as post-irradiation effects. However, the effects do not occur in dilute solutions. The iodine which can oxidize hydrogen peroxide to give oxygen seems to be I or I_2^-. Under the experimental conditions, all the hydroxyl radicals are scavenged by iodide ions and the following reactions, 21 and 22, do not occur, because the rate constants of these reactions are relatively slow (k_{21} and $k_{22}=4\times10^7\ \text{M}^{-1}\,\text{sec}^{-1}$):[26,27]

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \tag{21}$$

$$H + H_2O_2 \rightarrow OH + H_2O \tag{22}$$

From the results of the stationary concentrations of iodine and hydrogen peroxide in Fig. 1 and from the mechanisms proposed above, the following equations can be derived. As to the stationary state of iodine concentration:

$$G_{OH} + Ge^-_{aq}\frac{k_6[H_2O_2]}{k_5[H^+]+k_6[H_2O_2]+k_7[I_2]}$$

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[23] G. Czapski, J. Jortner and G. Stein, *J. Phys. Chem.*, **63**, 1769 (1959).

[24] M. Anbar, D. Meyerstein and P. Neta, ibid., **68**, 2967 (1964).

[25] G. Czapski and L. M. Dorfman, ibid., **68**, 1169 (1964).

[26] H. A. Schwarz, ibid., **66**, 255 (1962).

[27] J. K. Thomas, ibid., **67**, 2593 (1963).

$$= G_H + Ge^-_{aq}\frac{k_5[H^+]+k_7[I_2]}{k_5[H^+]+k_6[H_2O_2]+k_7[I_2]} + 2G(O_2) \qquad (23)$$

As to that of hydrogen peroxide:

$$G_{H_2O_2}=Ge^-_{aq}\frac{k_6[H_2O_2]}{k_5[H^+]+k_6[H_2O_2]+k_7[I_2]} + G(O_2) \qquad (24)$$

From Eqs. 23 and 24, the following relations can be obtained:

$$G_{OH} + 2G_{H_2O_2} = G_H + Ge^-_{aq} + 4G(O_2) \qquad (25)$$

In the potassium iodide solution of 5×10^{-4} M, most of the iodine produced is present in the form of I_2:

$$I_2 + I^- \rightleftarrows I_3^- \qquad (K = 7.2\times10^2)^{28)}$$

The values of k_5 and k_6 reported by Hart et al.[29] and $Ge^-_{aq}=2.8$ being used,[13,14,30] the rate constant of the reaction of hydrated electrons with iodine, $k_{e^-_{aq}+I_2}$, can be calculated from Eq. 24 to be 5.9×10^{10} M^{-1} sec,$^{-1}$ a value which is in good agreement with the value obtained by Hart et al.[31] using the pulse radiolysis technique.

On the other hand, in the deaerated solution of pH 5.3, $G(I_2)$ $G(H_2O_2)$ and $G(O_2)$, and the stationary concentrations of iodine and hydrogen peroxide are a little higher than those in the neutral solution. This may be due to the additional reaction of carbon dioxide with hydrated electrons.

$$CO_2 + e^-_{aq} \rightarrow CO_2^- \qquad (26)$$

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28) L. I. Grossweiner and M. S. Matheson, ibid., **61**, 1089 (1957).

29) S. Gordon, E. J. Hart, S. Matheson, J. Rabani and J. K. Thomas, *Discussions Faraday Soc.*, **36**, 193 (1963).

30) T. Sawai, unpublished data.

31) J. K. Thomas, S. Gordon and E. J. Hart, *J. Phys. Chem.*, **68**, 1524 (1964).